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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION 5  
230 SOUTH DEARBORN ST.  
CHICAGO, ILLINOIS 60604

REPLY TO THE ATTENTION OF:

**MEMORANDUM**

**5SCRL**

**DATE:** October 11, 1991

**SUBJECT:** Laboratory Evaluation of CH2M-Hill, Montgomery, Alabama  
for the Waukegan Coke Plant, IL Site

**FROM:** David A. Payne, Chief *DA Payne*  
Laboratory Scientific Support Section

**TO:** James Mayka, Chief  
IL/MN Section  
Remedial Response Branch

**ATTN:** Cindy Nolan

Ms. Cindy Nolan and Weston/ESAT evaluated the subject laboratory during August 1991, for PAH analysis (low-lead), in waters. The test procedure will not be used for soils. For the subject site's RI/FS, CLP Target Compound List (TCL) PAH compounds are to be reported. The attached report discusses indicator compounds; however, these should be interpreted as the five or more PAH compounds that are most toxic. During the lab evaluation these "indicator PAH's" were determined to be of acceptable analysis sensitivity for the RI/FS. Remaining PAH compounds of the TCL should be adequate sensitivity.

**Summary and Recommendations**

1. The low-level PAH test procedure of CH2M-Hill is generally acceptable for the indicator PAH's and remaining TCL PAH's in water. This is based on review of actual data packages for these analyses at the Montgomery laboratory.
2. The lab SOP that is part of the site QAPP should be upgraded to include both primary and secondary quant ions, and the rationale(s) for changing to alternate quant ions, for PAH compounds. Current detection limits should also be part of the lab's SOP.
3. CH2M-Hill should make their GC/MS tune documentation more systematic (see attached report), and the lab should consider decreasing the DFTPP concentration

for GC/MS tune checks to more closely resemble instrument calibration standard concentrations. This can not be a mandatory requirement since EPA does not have reference criteria available for 5 ng DFTPP.

4. Data packages should be upgraded to include initial calibration records, continuing calibrations, tuning data, etc. These will then provide evidential records comparable to the CLP SOW. This is a non-negotiable issue. An internal standard area summary form should also be added to the package.
5. CH2M-Hill should assure that they can resolve benzo(b) fluoranthene from benzo(k) fluoranthene on the GC column for the subject sites RI/FS study, or the sum of the two compounds results are to be used for the measurement of the most toxic PAH.
6. If sample extract results require dilution, a clear rationale must be provided in the case narrative for the data package as to why dilution was necessary and required PAH detection limits could not be obtained.

cc: G. Schupp, QA Section  
K. Khanna, WMD



**ENVIRONMENTAL SERVICES ASSISTANCE TEAM (ESAT)  
U.S.EPA REGION V**

**Laboratory Evaluation Report  
CH2MHILL  
Montgomery, Alabama**

**For**

**RCRA Facility Investigation  
Waukegan Coke Plant  
Waukegan, Illinois**

*Submitted to:*

David Payne  
LSSS Section Chief  
U.S.EPA Region V  
Central Regional Laboratory  
536 South Clark Street  
Chicago, IL 60605

*Submitted by:*

Kelly Head  
Roy F. Weston, Inc./ESAT Project  
536 South Clark Street  
Chicago, IL 60605

*Date: 15 August 1991  
TID No.: 059108-20  
Task No.: 5129*

## **Introduction**

The CH2MHILL Laboratory, Montgomery, Alabama was evaluated on 6 August 1991 for Polynuclear Aromatic Hydrocarbons (PAHs) at part per trillion (ppt) levels by GC/MS analysis full scan technique, in support of the RI/FS at the Waukegan Coke Plant site, Waukegan, IL.

ESAT reviewed the raw data packages supplied by CH2MHILL. In addition to the data review, ESAT discussed the procedures with the organic laboratory supervisor and various organic chemists. The Summary of the method and recommendations follows.

## **General Information**

Log books for standards preparation, instrument injection, and instrument maintenance appear to be current and properly maintained. Each GC/MS has two log books, one for instrument maintenance and a separate book for the injections onto the instrument.

During the review of the data package. The auditor noticed several items which should be corrected. Some ions used for quantitation were changed to an alternate ion. The SOP (incorporated into the QAPP for this site) should have a list of the primary and secondary quantitation ions included in the SOP, as well as the reasoning behind changing to the alternative ion. The alternate quantification ions should also be listed. The current Method Detection Limits should be included into the SOP as well. CH2MHILL needs to supply this information in the SOP. The Data users should have all of this information at their disposal.

There were also cross outs in the data package, which were not dated and initialed properly. Any corrections made in the laboratory should be initialed and dated with explanation for the changes.

## **Sample Preparation**

The method of sample preparation for PAHs is acceptable. CH2MHILL uses QC similar to the CLP semi-volatile method (internal standard, surrogate standard, and matrix spikes). A sample volume of 1.7 liters is measured into a 2-liter separatory funnel for extraction. The pH of the aliquot is adjusted to >10 and spiked with 100ng of surrogate standard compounds (SS). The sample is extracted three times with 60 mL of methylene chloride; the time period for each extraction is three minutes. The extract is concentrated to a volume of 1.0 mL. Prior to analysis of the extracts, the internal standard compounds (IS) are added and the extract is blown down to a final volume of 50 uL.

## **Instrument Tuning**

The laboratory tunes the GC/MS instrumentation to 50 ng of DFTPP to monitor daily instrument performance. The tune is verified every twelve hours of instrument operation. The tune reports are included in the final data packages in the CLP form V format.

The PAH data package which was reviewed, contained a DFTPP data file with two different ion ratios on two different forms. The first report form had a scan number present and supporting raw data, which was correct. The second form did not have a record of a scan number or any raw data. For the first form the DFTPP tuning was performed in accordance with the 2/88 SOW. The second form was compared to the 3/90 SOW criteria. The newest SOW specifies the scans to be used to meet the tuning criteria. CH2MHILL is trying to meet the new criteria, but is still following the old criteria. This explains why the ion ratios differed from one form to the other form.

### **Recommendation:**

- o All form Vs should have the scans present in the header information. There must be documentation to support the ion ratios. If the new ratios are not to be reported to the client do not include them in the final deliverables package.
- o The working calibration for this analysis is 0.1 to 3.0 ng. CH2MHILL is tuning the instrumentation with 50 ng of DFTPP. For the CLP routine analysis of semi-volatiles, the instrument is tuned to 50 ng of DFTPP. This is within the 20 to 160 ng working calibration. The laboratory may want to consider decreasing the DFTPP to a lower amount (25, 10, or 5ng).

## **Instrument Calibration**

A five point calibration ( 0.1, 0.5, 1.0, 2.0, and 3.0 ng/uL) is used to establish the working range of the instrument. The %RSDs must be less than 30% for the calibration check compounds (CCCs). The System Performance Check Compounds (SPCCs) must have a minimum mean relative response factor of 0.100. A calibration verification standard at 1.0 ug/mL is analyzed every 12 hours before samples can be analyzed. For the calibration verification the percent difference for the CCCs must not exceed 25% from the initial calibration. The SPCCs must have a minimum RF of 0.100. Both CCC and SPCC criteria must be met before samples can be analyzed. The compounds used as CCCs and SPCCs for this method are listed below.

**CCCs**

Naphthalene  
Acenaphthylene  
Dibenzothiophene  
Benzo(a)anthracene  
Benzo(a)pyrene

**SPCCs**

Quinoline  
Carbazole  
3-Methyl cholanthrene

No initial calibration data was present in the data package. CH2MHILL keeps all of the initial calibration, continuing calibration and tuning data in laboratory binders. The laboratory should include all pertinent data (sample preparation log, calibration log, tuning log, etc.) in the final data packages. If the data are ever used for litigation. All supporting data must be present. If they are not included with the first submission of data, the laboratory may be asked to retrieve the data at a later date. Therefore, it would be easier for anyone reviewing the data, if the data packages were self supporting when the data leaves the laboratory.

**Coelution of Isomers**

Several of the PAHs have isomers with similar mass spectra and coelution problems. Two of isomers pairs are benzo(a)anthracene/chrysene (228 m/z), and benzo(b)fluoranthene/benzo(k)fluoranthene (252 m/z). Both of the 228 m/z compounds are indicator compounds. The retention time difference between the apices of the 228 m/z peaks is about 0.05 minutes (30 scans). The benzo(b)fluoranthene is also an indicator compound. This compound is difficult to separate from the benzo(k)fluoranthene in a semi-volatile analysis, but these peaks can be resolved and they are reported separately in the CLP Method. These two compounds should be reported separately for this project.

**Sample Screening**

CH2MHILL screens all extracts by GC\FID prior to GC/MS analysis. This is done to prevent overloading of the GC/MS instrumentation. If a dilution is required for a sample. The Laboratory should include some supporting data as to why the dilution was necessary (FID chromatogram or the undiluted results). A sample requiring a one to forty dilution, should not report the high detection limits from the diluted sample. The Laboratory should try to analyze the sample at a decreased dilution and report the lowest detections limits possible.

**Quality Assurance and Quality Control**

The Quality Control (QC) for this method is similar to the CLP semi-volatile QC. The IS compounds are the same as the CLP semi-volatile IS compounds.

The concentration of the IS in the final extract is lower than the CLP semi-volatile analysis. The IS mixture is spiked into the extract before final blow down, to give a final concentration of 1ng/uL. No internal standard area summary form was included in the final data package. CH2MHILL does analyze an independent standard to verify the working calibration for the routine analysis (volatile and semi-volatile) but not for special analysis (PAHs).

**Recommendation:**

- o An internal standard summary form should be included in the data package.

The SS compounds used for sample spiking are; 1-fluoronaphthalene, nitrobenzene-d<sub>5</sub>, 2-fluorobiphenyl, and terphenyl-d<sub>14</sub>. 100ng of SS is added to the 1.7L sample before extraction. The Laboratory does keep QC charts for the SS recoveries. This information is stored on the LIMS. If more than two surrogate compounds exceeds  $\pm 3$  standard deviations the sample is scheduled for reanalysis. In the package which was reviewed, the samples were not spiked with the SS mixture. The Laboratory was able to re-extract the samples within the seven holding time. Thus saving the integrity of the analytical results.

CH2MHILL extracts a method blank with each set of samples. The blank did contain low level contamination of Naphthalene and Benzofuran. These contaminants were only present in the blank and not in the samples. These contaminants are probably from the blank water. If these compounds were from the methylene chloride or the glassware, they would be present in the samples as well. But they are not present in the samples. The reporting of positive results for these compounds should be watched carefully.

One set of matrix spike/matrix spike duplicate (MS/MSD) pair is analyzed for every twenty samples. Since this PAH analysis is specific for water matrix only. The comment "for every matrix " does not apply for the frequency of the MS/MSD analysis. The acceptable ranges for the MS percent recoveries is 10-130%. The Relative Percent Difference for the MS/MSD must be  $\leq 25\%$ . The compounds used for the MS/MSD analysis are listed below.

1H-Indene	Phenanthrene
Naphthalene	Carbazole
2-Methylnaphthalene	Pyrene
Acenaphthene	Benzo(e)pyrene
	Indeno(1,2,3-cd)pyrene

**Recommendations:**

- o Five of the PAHs are considered to be carcinogenic and are typically used as indicators for field cleanup procedures. The following five compounds should be incorporated into the MS spiking solution; Chrysene, Naphthalene, Benzo(a)anthracene, Benzo(b)fluoranthene, and Benzo(a)pyrene.
- o Since Benzo(b)fluoranthene is important to the field work, the laboratory should report the Benzo(b)fluoranthene and Benzo(k)fluoranthene as separate parameters and not as Benzo(b+k)fluoranthene combined. CH2MHILL should be capable of achieving the peak resolution.

*Kelly D. Head*  
*P. Henley*